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(54) **Bleach activation**

(57) A bleach and oxidation catalyst is provided comprising a catalytically active iron complex including a defined pentadentate nitrogen containing ligand. This type of iron complex can activate hydrogen peroxide or peroxy acids and was found to have favourable stain

removal and remarkable dye transfer inhibition properties. In addition, a considerably improved stability of these iron complex compounds in alkaline aqueous environment has been obtained, in particular at the peroxy compound concentrations generally present in the fabric washing liquor.

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DescriptionField of the Invention

- 5 [0001] The invention relates to activation of bleaches employing peroxy compounds including hydrogen peroxide or hydrogen peroxide adducts, which liberate hydrogen peroxide in aqueous solution, and peroxy acids (or precursors thereof); to compounds that activate or catalyse peroxy compounds; to bleach compositions, including detergent bleach compositions, which contain a catalyst for peroxy compounds; and to processes for bleaching and/or washing substrates using the aforementioned types of compositions.
- 10 [0002] In particular, the present invention is concerned with the novel use of iron compounds as catalysts for the bleach activation of peroxy compounds.

Background of the Invention.

- 15 [0003] Peroxide bleaching agents for use in laundering have been known for many years. Such agents are effective in removing stains, such as tea, fruit, and wine stains, from clothing at or near boiling temperatures. The efficacy of peroxide bleaching agents drops off sharply at temperatures below 60°C.
- [0004] Previous patent applications dealt with environmentally acceptable manganese ions and complexes. US-A-4,728,455 discusses the use of Mn(III)-gluconate as peroxide bleach catalyst with high hydrolytic and oxidative stability; relatively high ratios of ligand (gluconate) to Mn are, however, needed to obtain the desired catalytic system. Moreover, the performance of these Mn-based catalysts is inadequate when used for bleaching in the low-temperature region of about 20°-40°C, and they are restricted in their efficacy to remove a wide range of stains.
- 20 [0005] In several patent documents, for instance EP-A-458,379, novel triazacyclononane-based manganese complexes are disclosed, which display a high catalytic oxidation activity at low temperatures that is particularly suitable for bleaching purposes. A major improvement of the bleaching activity could be obtained by virtue of the fact that these compounds are stable under washing conditions, e.g. high alkalinity and oxidizing environment (as a result of the presence of hydrogen peroxide or peroxy acids).
- 25 [0006] In addition to the above-mentioned stain removal, dye transfer is a well-known problem in the art and has been addressed in various ways. For instance, an improved dye transfer inhibition has been obtained by using Fe-porphyrin and Fe-phthalocyanine complexes (see EP-A-537,381, EP-A-553,607, EP-A-538,228).
- [0007] It is well known that the stability of Fe-co-ordination complexes in alkaline aqueous media in the presence of peroxide compounds is very poor. In BP-A-537,381 and EP-A-553,607, methods are disclosed for improvement in this respect.
- 30 [0008] This poor stability of Fe-co-ordination species has resulted in the necessity of very low concentrations of peroxide and, additionally, the use of polymers (see EP-A-538,228). These measures, however, only reduce the negative effects of the above-indicated poor stability to some extent and do not provide a complete solution to this problem.
- [0009] In WO-A-9534628, it has been shown that the use of iron compounds containing pentadentate nitrogen-containing ligands, in particular the use of N,N-bis(pyridin-2-ylmethyl)-bis(pyridin-2-yl)methylamine, as bleaching and oxidation catalysts, resulted in a favourable bleaching activity, dye bleaching activity and oxidation activity in general.
- 40 [0010] We have now surprisingly found that a significantly improved catalytic oxidation activity of the Fe-coordination complex can be obtained by substituting the H-atom of the C-H group of the methylamine moiety present in the ligands according to WO-A-9534628, by other groups.
- [0011] As a consequence, these new iron compounds were found to provide favourable stain removal in the presence of hydrogen peroxide or peroxy acids. Furthermore, an improved bleaching activity has been particularly noted in alkaline aqueous solutions containing peroxy compounds at concentrations generally present in the wash liquor during the fabric washing cycle.
- 45 [0012] Additionally, these new iron compounds exhibit remarkable dye transfer inhibition properties, and, alternatively, oxidation of organic substrates such as olefins, alcohols and unactivated hydrocarbons.

50 Definition of the Invention

[0013] In one aspect, the present invention provides a bleach and oxidation catalyst comprising an Fe-complex having formula (A):

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or precursors thereof, in which

Fe is iron in the II, III, IV or V oxidation state;

X represents a coordinating species such as H₂O, ROH, NR₃, RCN, OH, OOH, OOR, RS⁻, RO⁻, RCOO⁻, OCN⁻, SCN⁻, N₃⁻, CN⁻, F⁻, Cl⁻, Br⁻, I⁻, O²⁻, NO₃⁻, NO₂⁻, SO₄²⁻, SO₃²⁻, PO₄³⁻ or aromatic N donors such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles and thiazoles with R being H, optionally substituted alkyl or optionally substituted aryl;

n is an integer ranging from 0-3;

Y is a counter ion, the type of which is dependent on the charge of the complex;

q = Z/[charge Y];

Z denotes the charge of the complex and is an integer which can be positive, zero or negative; if Z is positive, Y is an anion such as F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, BPh₄⁻, ClO₄⁻, BF₄⁻, PF₆⁻, RSO₃⁻, RSO₄⁻, SO₄²⁻, CF₃SO₃⁻ or RCOO⁻; if Z is negative, Y is a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation; and L represents a ligand of general formula (B):



which contains at least five nitrogen atoms and in which the substituent groups R₁-R₅ are independently selected from hydrogen, hydroxy, halogen, nitroso, formyl, carboxyl, and esters and salts thereof, carbamoyl, sulfo, and esters and salts thereof, sulfamoyl, nitro, amino, C₀-C₂₀-alkyl-hydroxy, C₀-C₂₀-alkyl-halogen, C₀-C₂₀-alkyl-nitroso, C₀-C₂₀-alkyl-formyl, C₀-C₂₀-alkyl-carboxyl, and esters and salts thereof, C₀-C₂₀-alkyl-carbamoyl, C₀-C₂₀-alkyl-sulfo, and esters and salts thereof, C₀-C₂₀-alkyl-sulfamoyl, C₀-C₂₀-alkyl-amino, C₀-C₂₀-alkylaryl, C₀-C₂₀-alkylheteroaryl, C₀-C₂₀ alkyl, C₀-C₈ alkoxy, carbonyl-C₀-C₆-alkoxy, and aryl-C₀-C₆-alkyl, provided that R₁ does not represent hydrogen.

[0014] In another aspect, the present invention provides a bleaching composition comprising a peroxy compound bleach preferably selected from hydrogen peroxide, hydrogen peroxide-liberating or -generating compounds, peroxyacids and their salts, and mixtures thereof, optionally together with peroxyacid bleach precursors, and a catalyst according to the present invention.

Detailed Description of the Invention

[0015] Generally, the Fe-complex catalyst of the invention may be used in a bleaching system comprising a peroxy compound or a precursor thereof, and may be suitable for use in the washing and bleaching of substrates including laundry, dishwashing and hard surface cleaning. Alternatively, the Fe-complex catalyst of the invention may be used for bleaching in the textile, paper and woodpulp industries, as well as in waste water treatment.

[0016] As already stated, an advantage of the Fe-complex catalysts according to the present invention is that they exhibit a remarkably high oxidation activity in alkaline aqueous media in the presence of peroxy compounds.

[0017] A second advantage of the new Fe-complex catalysts of the invention is that they show good bleaching activity at a broader pH range (generally pH 6-11) than those observed for the previously disclosed iron complexes. Their performance was especially improved at pH of around 10. This advantage may be particularly beneficial in view of the current detergent formulations that employ rather alkaline conditions, as well as the tendency to shift the pH during fabric washing from alkaline (typically, a pH of 10) to more neutral values. Furthermore, this advantage may be beneficial when using the present iron complex catalyst in machine dishwash formulations.

[0018] An additional advantage is that such compounds are active as dye-transfer inhibition agents, as shown in Example 5.

[0019] Another advantage is that the catalysts of the invention have a relatively low molecular weight and, consequently, are very weight-effective.

[0020] Precursors of the active Fe-complex catalysts of the invention can be any iron coordination complex, which, under fabric washing conditions, is transformed into the active iron complex of general formula (A). Alternatively, the precursor of the Fe-complex of the invention can be a mixture of an iron salt, such as Fe(NO₃)₃, and the ligand L.

[0021] A preferred class of ligands is that of compounds of general formula (B), in which R₂, R₃, R₄, R₅ are inde-

pendently chosen from C₀-C₅ alkyl substituted with nitrogen-containing heterocyclic aromatic groups, such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, thiazoles, triazoles and pyrimidines, in particular pyridines, and in which the substituent group R₁ represents any group other than hydrogen, e.g. hydroxy, halogen, nitroso, formyl, carboxyl, and esters and salts thereof, carbamoyl, sulfo, and esters and salts thereof, sulfamoyl, nitro, amino, C₀-C₂₀-alkyl-hydroxy, C₀-C₂₀-alkyl-halogen, C₀-C₂₀-alkyl-nitroso, C₀-C₂₀-alkyl-formyl, C₀-C₂₀-alkyl-carboxyl, and esters and salts thereof, C₀-C₂₀-alkyl-carbamoyl, C₀-C₂₀-alkyl-sulfo, and esters and salts thereof, C₀-C₂₀-alkyl-sulfamoyl, C₀-C₂₀-alkyl-amino, C₀-C₂₀-alkylaryl, C₀-C₂₀-alkylheteroaryl, C₀-C₂₀ alkyl, C₀-C₈ alkoxy, carbonyl-C₀-C₆-alkoxy, aryl-C₀-C₆-alkyl, whereby the carbamoyl, sulfamoyl and amino groups are optionally further substituted by any other group.

[0022] A more preferred class of ligands is that of compounds of general formula (B), in which the substituent group R₁ is selected from C₀-C₂₀ alkylaryl, C₀-C₂₀ alkylheteroaryl, and C₀-C₂₀ alkyl, and in which the substituent groups R₂, R₃, R₄, and R₅ are independently chosen from C₀-C₅ alkyl substituted with a pyridine ring.

[0023] Examples of preferred ligands in their simplest forms are:

N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(pyrazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
 N,N-bis(pyrazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(imidazol-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
 N,N-bis(imidazol-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(1,2,4-triazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
 N,N-bis(1,2,4-triazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyrazol-1-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyrazol-1-yl)-2-phenyl-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(imidazol-2-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(imidazol-2-yl)-2-phenyl-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(1,2,4-triazol-1-yl)-1-aminoethane;
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(1,2,4-triazol-1-yl)-1-aminoethane;

[0024] More preferred ligands are:

N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(4-sulfonic acid-phenyl)-1-aminoethane,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-2-yl)-1-aminoethane,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-3-yl)-1-aminoethane,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-4-yl)-1-aminoethane,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-4-yl)-1-aminoethane,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-3-yl)-1-aminoethane,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-2-yl)-1-aminoethane.

[0025] The most preferred ligands are:

N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, hereafter referred to as MeN₄Py,
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane, hereafter referred to as BzN₄Py.

[0026] Suitable counter ions are those which give rise to the formation of storage-stable solids. Combination of the preferred iron complexes with the counter ion Y preferably involves counter ions selected from RCOO⁻, BPh₄⁻, ClO₄⁻, BF₄⁻, PF₆⁻, RSO₃⁻, RSO₄⁻, SO₄²⁻, NO₃⁻, F⁻, Cl⁻, Br⁻, I⁻ wherein R=H, optionally substituted phenyl, naphthyl or C₁-C₄ alkyl. Preferred co-ordinating species X are selected from CH₃CN, pyridine, H₂O, Cl⁻, OR⁻, and OOH⁻, wherein R=H, optionally substituted phenyl, naphthyl or C₁-C₄ alkyl.

[0027] The effective level of the Fe-complex catalyst, expressed in terms of parts per million (ppm) of iron in an aqueous bleaching solution, will normally range from 0.001 ppm to 100 ppm, preferably from 0.01 ppm to 20 ppm, most preferably from 0.1 ppm to 10 ppm. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp bleaching. The lower range levels are preferably used in domestic laundry operations.

The detergent bleach composition

[0028] The bleaching composition of the invention has particular application in detergent formulations, to form a new and improved detergent bleach composition within the purview of the invention comprising a peroxy compound bleach as defined above, the aforesaid Fe-complex catalyst having general formula (A), a surface-active material and a detergent builder.

[0029] The Fe-complex catalyst will be present in the detergent bleach composition of the invention in amounts so as to provide the required level in the wash liquor. Generally, the Fe-complex catalyst level in the detergent bleach composition corresponds to an iron content of from 0.0005% to 0.5% by weight. When the dosage of detergent bleach composition is relatively low, e.g. about 1-2 g/l, the Fe content in the formulation is suitably 0.0025 to 0.5%, preferably 0.005 to 0.25% by weight. At higher product dosages, as used e.g. by European consumers, the Fe content in the formulation is suitably 0.0005 to 0.1%, preferably 0.001 to 0.05% by weight.

[0030] Detergent bleach compositions of the invention are effective over a wide pH-range of between 7 and 13, with optimal pH-range lying between 8 and 11.

The peroxy bleaching compound

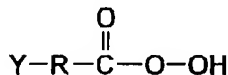
[0031] The peroxy bleaching compound may be a compound which is capable of yielding hydrogen peroxide in aqueous solution. Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates persulfates and persulphates. Mixtures of two or more such compounds may also be suitable.

[0032] Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons. The amount thereof in the composition of the invention usually will be within the range of about 5-35 % by weight, preferably from 10-25 % by weight.

[0033] Another suitable hydrogen peroxide generating system is a combination of a C₁-C₄ alcohol oxidase and a C₁-C₄ alcohol, especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in WO-A-9507972, which is incorporated herein by reference.

[0034] Alkylhydroxy peroxides are another class of peroxy bleaching compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

[0035] Organic peroxyacids may also be suitable as the peroxy bleaching compound. Such materials normally have the general formula:



wherein R is an alkyl- or alkylidene- or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or COOOH group or a quaternary ammonium group.

[0036] Typical monoperoxy acids useful herein include, for example:

- (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy- α -naphthoic acid;
- (ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxy lauric acid, peroxy stearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and
- (iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

[0037] Typical diperoxyacids useful herein include, for example:

- (iv) 1,12-diperoxydodecanedioic acid (DPDA);
- (v) 1,9-diperoxyazelaic acid;
- (vi) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (vii) 2-decyldiperoxybutane-1,4-dioic acid; and
- (viii) 4,4'-sulphonylbis(peroxybenzoic acid).

[0038] Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS).

If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10% by weight, preferably from 4-8 % by weight.

[0039] All these peroxy compounds may be utilized alone or in conjunction with a peroxyacid bleach precursor and/or an organic bleach catalyst not containing a transition metal. Generally, the bleaching composition of the invention

can be suitably formulated to contain from 2 to 35% , preferably from 5 to 25% by weight, of the peroxy bleaching agent.

[0040] Peroxyacid bleach precursors are known and amply described in literature, such as in GB-A-836988; GB-A-

864,798; GB-A-907,356; GB-A-1,003,310 and GB-A-1,519,351; DE-A-3,337,921; EP-A-0,185,522; EP-A-0,174,132;

EP-A-0,120,591; and US-A-1,246,339; US-A-3,332,882; US-A-4,128,494; US-A-4,412,934 and US-A-4,675,393.

[0041] Another useful class of peroxyacid bleach precursors is that of the cationic i.e. quaternary ammonium substituted peroxyacid precursors as disclosed in US-A-4,751,015 and US-A-4,397,757, in EP-A-0,284,292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are:

2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphophenyl carbonate chloride- (SPCC);

N-octyl,N,N-dimethyl-N₁₀-carbophenoxy decyl ammonium chloride - (ODC);

3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and

N,N,N-trimethyl ammonium toluoyloxy benzene sulphonate.

[0042] A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520; EP-A-458,396 and EP-A-464,880.

[0043] Any one of these peroxyacid bleach precursors can be used in the present invention, although some may be more preferred than others.

[0044] Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

[0045] Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N',N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; 2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphophenyl carbonate chloride (SPCC); trimethyl ammonium toluoyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyloxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

[0046] The precursors may be used in an amount of up to 12 %, preferably from 2-10% by weight, of the composition.

[0047] As an alternative to the above described peroxide generating systems, molecular oxygen may be used as the oxidant.

The surface-active material

[0048] The detergent bleach composition according to the present invention generally contains a surface-active material in an amount of from 10 to 50% by weight.

[0049] Said surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

[0050] Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C₈-C₁₈) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C₉-C₁₀) benzene sulphonates, particularly sodium linear secondary alkyl (C₁₀-C₁₅) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C₉-C₁₈) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane mono-sulphonates such as those derived by reacting alpha-olefins (C₈-C₂₀) with sodium bisulphite and those derived by reaction paraffins with SO₂ and Cl₂ and then hydrolysing with a base to produce a random sulphonate; sodium an ammonium C₇-C₁₂ dialkyl sulphosuccinates; and olefin sulphonates which term is used to describe material made by reacting olefins, particularly C₁₀-C₂₀ alpha-olefins, with SO₃ and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C₁₀-C₁₅) alkylbenzene sulphonates, sodium (C₁₆-C₁₈) alkyl ether sulphates.

[0051] Examples of suitable nonionic surface-active compounds which may be used, preferably together with the

anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6 - C_{22}) phenols, generally 5-25 EO, *i.e.* 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic (C_8 - C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

[0052] Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

[0053] As disclosed by EP-A-544,490, the performance of the hereinbefore described bleach catalyst may be dependent upon the active detergent system and the builder system present in the detergent bleach composition of the invention.

[0054] The detergent bleach composition of the invention will preferably comprise from 1-15 % wt of anionic surfactant and from 10-40 % by weight of nonionic surfactant. In a further preferred embodiment the detergent active system is free from C_{16} - C_{12} fatty acids soaps.

The detergency builder

[0055] The composition of the invention normally and preferably also contains a detergency builder in an amount of from about 5-80 % by weight, preferably from about 10-60 % by weight.

[0056] Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

[0057] Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in US-A-4,144,226 and US-A-4,146,495.

[0058] Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

[0059] Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, *e.g.* zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0384070.

[0060] In particular, the compositions of the invention may contain any one of the organic and inorganic builder materials, though, for environmental reasons, phosphate builders are preferably omitted or only used in very small amounts.

[0061] Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and the water-insoluble crystalline or amorphous aluminosilicate builder material, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

[0062] It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferable not more than 2.5 % by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Other ingredients

[0063] Apart from the components already mentioned, the detergent bleach composition of the invention can contain any of the conventional additives in amounts of which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilizers, such as phosphonic acid derivatives (*i.e.* Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulphate and sodium silicate; and usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

[0064] When using a hydrogen peroxide source, such as sodium perborate or sodium percarbonate, as the bleaching compound, it is preferred that the composition contains not more than 5 % by weight of a carbonate buffer, expressed as sodium carbonate, more preferable not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

[0065] Of the additives, transition metal sequestrants such as EDTA and the phosphonic acid derivatives, *e.g.* ethylene diamine tetra-(methylene phosphonate)-EDTMP- are of special importance, as not only do they improve the

stability of the catalyst/H₂O₂ system and sensitive ingredients, such as enzymes, fluorescent agents, perfumes and the like, but also improve the bleach performance, especially at the higher pH region of above 10, particularly at pH 10.5 and above.

[0066] The invention will now be further illustrated by way of the following non-limiting examples:

Example 1

Preparation of MeN₄Py ligand

[0067] The precursor N₄Py.HClO₄ was prepared as follows:

To pyridyl ketone oxim (3 g, 15.1 mmol) was added ethanol (15 ml), concentrated ammonia solution (15 mL) and NH₄OAc (1.21 g, 15.8 mmol). The solution was warmed until reflux. To this solution was added 4.64 g Zn in small portions. After the addition of all Zn, the mixture was refluxed for 1 hour and allowed to cool to ambient temperature. The solution was filtered and water (15 ml) was added. Solid NaOH was added until pH >> 10 and the solution was extracted with CH₂Cl₂ (3 x 20 ml). The organic layers were dried over Na₂SO₄ and evaporated until dryness. Bis(pyridin-2-yl)methylamine (2.39 g, 12.9 mmol) was obtained as a colourless oil in 86% yield, showing the following analytical characteristics:

¹H NMR (360 MHz, CDCl₃): δ 2.64 (s, 2H, NH₂), 5.18 (s, 1H, CH), 6.93 (m, 2H, pyridine), 7.22 (m, 2H, pyridine), 7.41 (m, 2H, pyridine), 8.32 (m, 2H, pyridine); ¹³C NMR (CDCl₃): δ 62.19 (CH), 121.73 (CH), 122.01 (CH), 136.56 (CH), 149.03 (CH), 162.64 (Cq).

[0068] To picolylchloride hydrochloride (4.06 g, 24.8 mmol) was added, at 0°C, 4.9 ml of a 5N NaOH solution. This emulsion was added by means of a syringe to bis(pyridin-2-yl)methylamine (2.3 g, 12.4 mmol) at 0°C. Another 5 ml of a 5N NaOH solution was added to this mixture. After warming to ambient temperature, the mixture was stirred vigorously for 40 hrs. The mixture was put in an ice bath and HClO₄ was added until pH < 1, whereupon a brown solid precipitated.

The brown precipitate was collected by filtration and recrystallized from water. While stirring, this mixture was allowed to cool to ambient temperature, whereupon a light-brown solid precipitated which was collected by filtration and washed with cold water and air-dried (1.47 g).

[0069] From 0.5 g of the perchlorate salt of N₄Py prepared as described above, the free amine was obtained by precipitating the salt with 2N NaOH and subsequently by extraction with CH₂Cl₂. To the free amine was added under argon 20 ml of dry tetrahydrofuran freshly distilled from LiAlH₄. The mixture was stirred and cooled to -70 °C by an alcohol / dry ice bath. Now 1 ml of 2.5 N butyllithium solution in hexane was added giving an immediate dark red colour. The mixture was allowed to warm to -20 °C and now 0.1 ml of methyl iodide was added. The temperature was kept to -10 °C for 1 hour. Subsequently 0.5 g of ammonium chloride was added and the mixture was evaporated in vacuo. To the residue water was added and the aqueous layer was extracted with dichloromethane. The dichloromethane layer was dried on sodium sulfate, filtered and evaporated giving 0.4 g residue. The residue was purified by crystallisation from ethyl acetate and hexane giving 0.2 g of creamish powder (50% yield) showing the following analytical characteristics:

¹H NMR (400 MHz, CDCl₃): δ (ppm) 2.05 (s, 3H, CH₃), 4.01 (s, 4H, CH₂), 6.92 (m, 2H, pyridine), 7.08 (m, 2H, pyridine), 7.39 (m, 4H pyridine), 7.60 (m, 2H, pyridine), 7.98 (d, 2H, pyridine), 8.41 (m, 2H pyridine), 8.57 (m, 2H, pyridine). ¹³C NMR (100.55 MHz, CDCl₃): δ (ppm) 21.7 (CH₃), 58.2 (CH₂), 73.2 (Cq), 121.4 (CH), 121.7 (CH), 123.4 (CH), 123.6 (CH), 136.0 (CH), 148.2 (Cq), 148.6 (Cq), 160.1 (Cq), 163.8 (Cq).

[0070] Subsequently [(MeN₄Py)Fe(CH₃CN)](ClO₄)₂, hereinafter referred to as Fe(MeN₄Py), was prepared as follows:

[0071] To a solution of 0.27 g of MeN₄Py in 12 ml of a mixture of 6 ml acetonitrile and 6 ml methanol was added 350 mg Fe(ClO₄)₂·6H₂O immediately a dark red colour formed. To the mix was added now 0.5 g of sodium perchlorate and a orange red precipitate formed immediately. After 5 minutes stirring and ultrasonic treatment the precipitate was isolated by filtration and dried in vacuo at 50°C. In this way 350 mg of an orange red powder was obtained in 70% yield showing the following analytical characteristics: ¹H NMR (400 MHz, CD₃CN): δ (ppm) 2.15, (CH₃CN), 2.28 (s, 3H, CH₃), 4.2 (ab, 4H, CH₂), 7.05 (d, 2H, pyridine), 7.38 (m, 4H, pyridine), 7.71 (2t, 4H pyridine), 7.98 (t, 2H, pyridine), 8.96 (d, 2H pyridine), 9.06 (m, 2H, pyridine).

UV/Vis (acetonitrile) [λ_{max}, nm (ε, M⁻¹ cm⁻¹): 381 (8400), 458 nm (6400).

Anal. Calcd for C₂₅H₂₆Cl₂FeN₆O₈: C, 46.11; H, 3.87; N, 12.41; Cl, 10.47; Fe, 8.25. Found: C, 45.49; H, 3.95; N, 12.5; Cl, 10.7; Fe, 8.12.

Mass-ESP (cone voltage 17V in CH₃CN): m/z 218.6 [MeN₄PyFe]²⁺; 239.1 [MeN₄PyFeCH₃CN]²⁺.

Example 2Preparation of BzN_4Py ligand

[0072] To 1 g of the N_4Py ligand prepared as described above, 20 ml of dry tetrahydrofuran freshly distilled from LiAlH_4 , was added under argon. The mixture was stirred and cooled to -70°C by an alcohol / dry ice bath. Now 2 ml of 2.5 N butyllithium solution in hexane was added giving an immediate dark red colour. The mix was allowed to warm to -20°C and now 0.4 ml of benzyl bromide was added. The mixture was allowed to warm up to 25°C and stirring was continued over night. Subsequently 0.5 g of ammonium chloride was added and the mixture was evaporated in vacuo. To the residue water was added and the aqueous layer was extracted with dichloromethane. The dichloromethane layer was dried on sodium sulfate, filtered and evaporated giving 1 g brown oily residue. According to NMR spectroscopy, the product was not pure but contained no starting material (N_4Py). The residue was used without further purification.

[0073] Subsequently $[(\text{BzN}_4\text{Py})\text{Fe}(\text{CH}_3\text{CN})](\text{ClO}_4)_2$, hereinafter referred to as $\text{Fe}(\text{BzN}_4\text{Py})$, was prepared as follows:

[0074] To a solution of 0.2 g of the residue obtained by the previous described procedure in 10 ml of a mixture of 5 ml acetonitrile and 5 ml methanol was added 100 mg $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ immediately a dark red colour formed. To the mix was added now 0.25 g of sodium perchlorate and ethylacetate was allowed to diffuse into the mixture overnight. Some red crystals were formed which were isolated by filtration and washed with methanol. In this way 70 mg of a red powder was obtained showing the following analytical characteristics:

[0075] ^1H NMR (400 MHz, CD_3CN): δ (ppm) 2.12, (s, 3H, CH_3CN), 3.65 + 4.1 (ab, 4H, CH_2), 4.42 (s, 2H, CH_2 -benzyl), 6.84 (d, 2H, pyridine), 7.35 (m, 4H, pyridine), 7.45 (m, 3H, benzene) 7.65 (m, 4H benzene + pyridine), 8.08 (m, 4H, pyridine), 8.95 (m, 4H pyridine).

UV/Vis (acetonitrile) [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 380 (7400), 458 nm (5500).

Mass-ESP (cone voltage 17V in CH_3CN): m/z 256.4 $[\text{BzN}_4\text{Py}]^{2+}$; 612 $[\text{BzN}_4\text{PyFeClO}_4]^+$

Example 3

[0075] The bleaching activity of the Fe-catalysts prepared according to Example 1 and 2, was demonstrated in the presence of hydrogen peroxide on standard tea-stained (BC-1) cotton test cloths.

[0076] The experiments were carried out at 40°C and at a pH of 10 in a temperature-controlled glass beaker equipped with a magnetic stirrer, thermocouple and a pH electrode.

[0077] Two pieces of test cloth were stirred for 30 minutes in 1 liter of a 8.6×10^{-3} mol/l hydrogen peroxide solution in millipore water, containing concentrations of the compounds as indicated in Table 1. After rinsing with demineralised water, the test cloths were dried for 7 minutes in a microwave oven. The reflectance (R_{460}^*) of the test cloths was measured on a Minolta® CM-3700d spectrophotometer including UV-filter before and after treatment. The difference (ΔR_{460}^*) between both reflectance values thus obtained gives a measure of the bleaching performance, i.e. higher ΔR_{460}^* values correspond to an improved bleaching performance.

TABLE 1

	conc. Fe	ΔR_{460}^*
	(mol/l)	(at pH=10)
blank	-	6.5
$\text{Fe}(\text{NO}_3)_3$	10×10^{-6}	6.2
$\text{Fe}(\text{N}_4\text{Py})$	10×10^{-6}	12.0
$\text{Fe}(\text{MeN}_4\text{Py})$	10×10^{-6}	15.8
$\text{Fe}(\text{BzN}_4\text{Py})$	10×10^{-6}	17.3

[0078] In Table 1, $\text{Fe}(\text{MeN}_4\text{Py})$ and $\text{Fe}(\text{BzN}_4\text{Py})$ refer to the Fe-catalysts prepared according to Examples 1 and 2, and $\text{Fe}(\text{N}_4\text{Py})$ to the non-methylated analogue as described in WO-A-9534628, The blank and $\text{Fe}(\text{NO}_3)_3$ experiment were used as control.

[0079] These measurements show that significantly improved bleaching performance is obtained with $\text{Fe}(\text{MeN}_4\text{Py})$ and $\text{Fe}(\text{BzN}_4\text{Py})$ as compared to $\text{Fe}(\text{N}_4\text{Py})$ as catalyst.

Example 4

[0080] The bleaching activity of the $\text{Fe}(\text{MeN}_4\text{Py})$ catalyst prepared according to Example 1 was demonstrated in the

presence of a detergent formulation on standard tea-stained (BC-1) cotton test cloths.

[0081] The detergent formulation contained the following ingredients and was dosed (in water) as indicated in Table 2.

TABLE 2

Detergent formulation used for the bleaching experiments with Fe(MeN ₄ Py)	
Ingredient	Dosage (g/l)
Sodium linear alkylbenzene sulphonate (LAS)	0.60
Sodium triphosphate (STP)	0.36
Sodium carbonate	0.44
Sodium disilicate	0.20
Sodium sulphate	0.67
Sodium perborate monohydrate	0.20
Tetraacetyleneethylene diamine (TAED)	0.06 ¹⁾
Fe(MeN ₄ Py)	<0.01 ²⁾
enzymes, fluorescer, SCMC, minors, moisture	0.19

¹⁾ Only for experiment A

²⁾ Only for experiment B

[0082] The experiments were carried out at 25°C and at a pH of around 10 (pH of the wash liquor) by using water of 4 °F (Ca:Mg= 4:1) in a temperature-controlled glass beaker equipped with a magnetic stirrer, thermocouple and a pH electrode.

[0083] Two pieces of test cloth were stirred for 30 minutes in 1 liter of the above detergent formulation yielding *in situ*.

- * in experiment A: 1.5×10^{-3} mol/l hydrogen peroxide and 0.5×10^{-3} mol/l peroxyacetic acid; and
- * in experiment B: 2×10^{-3} mol/l hydrogen peroxide containing 1×10^{-5} mol/l Fe(MeN₄Py).

[0084] After rinsing with demineralised water, the test cloths were dried for 7 minutes in a microwave oven. The reflectance (R_{460}^*) of the test cloths was measured on a Minolta® CM-3700d spectrophotometer including UV-filter before and after treatment. The difference (ΔR_{460}^*) between both reflectance values thus obtained gives a measure of the bleaching performance, *i.e.* higher ΔR_{460}^* values correspond to an improved bleaching performance.

Experiment A: 4.0 ΔR_{460}^* bleaching units

Experiment B: 6.7 ΔR_{460}^* bleaching units

[0085] These measurements show that significantly improved bleaching performance is obtained with Fe(MeN₄Py)/H₂O₂ in representative detergent formulation, compared to peroxyacetic acid/H₂O₂ in the same detergent formulation.

Example 5

[0086] The dye oxidation activity of the Fe-catalysts prepared according to Examples 1 and 2 was demonstrated in the presence of hydrogen peroxide on a dye known as Acid Red 88.

[0087] The experiments were carried out at 40 °C at pH=10 in a 1 cm cuvet in the presence of 8.6×10^{-3} mol/l hydrogen peroxide and 6×10^{-5} mol/l Acid Red 88. The absorbance at 503 nm (A_{503}), which is the maximum of the characteristic visible absorption of the dye in aqueous media, was measured at t=0 and t=30 minutes. The ΔA_{503} value given in the table is a measure of the dye bleaching activity: $\Delta A_{503} = 1 - (A_{503}(t=30)/A_{503}(t=0 \text{ min}))$, expressed in %.

[0088] A higher ΔA_{503} value represent a better dye bleaching activity.

TABLE 3

	conc. (mol/l)	pH 10	pH 8
		ΔA_{503}	ΔA_{503}
blank	-	15%	2 %
Fe(NO ₃) ₃	5×10^{-6}	16 %	2 %
Fe(MeN ₄ Py)	5×10^{-6}	26 %	79 %
Fe(BzN ₄ Py)	5×10^{-6}	35 %	86 %

[0089] Fe(MeN₄Py) and Fe(BzN₄Py) in Table 2 refer to the Fe-catalyst prepared according to Examples 1 and 2. The blank and Fe(NO₃)₃ experiment were used as controls.

[0090] These measurements show that improved dye oxidation performance is obtained when Fe(MeN₄Py) and Fe(BzN₄Py) are used as catalysts, especially at pH 8.

Example 6

[0091] The oxidation activity of Fe(MeN₄Py) catalyst, prepared according to example 1, was demonstrated in the presence of hydrogen peroxide on a range of organic substrates. The experiments were carried out at ambient temperature in acetone. The concentration of the Fe catalyst was 7.7x10⁻⁴ M and the ratio catalyst/H₂O₂/substrate was 1/100/1000. The turnover numbers indicated in Table 4 represent the number of molecules formed per molecule of catalyst as determined after the indicated time of the reaction by using gas chromatography. In a blank experiment or in the presence of Fe(NO₃)₃, essentially no oxidation products could be detected.

TABLE 4

substrate	product (turnover number)	reaction time
cyclohexene	2-cyclohexen-1-ol (9) 2-cyclohexen-1-one (3) cyclohexene epoxide (0)	30 minutes
cyclohexane	cyclohexanol (11) cyclohexanone (6)	30 minutes

Claims

1. A bleach and oxidation catalyst comprising an Fe-complex having formula (A):



or precursors thereof, in which

Fe is iron in the II, III, IV or V oxidation state;

X represents a co-ordinating species such as H₂O, ROH, NR₃, RCN, OH⁻, OOH⁻, RS⁻, RO⁻, RCOO⁻, OCN⁻, SCN⁻, N₃⁻, CN⁻, F⁻, Cl⁻, Br⁻, I⁻, O²⁻, NO₃⁻, NO₂⁻, SO₄²⁻, SO₃²⁻, PO₄³⁻ or aromatic N donors such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles and thiazoles with R being H, optionally substituted alkyl or optionally substituted aryl;

n is an integer number ranging from 0-3;

Y is a counter ion, the type of which is dependent on the charge of the complex;

z denotes the charge of the complex and is an integer which can be positive, zero or negative; if z is positive, Y is an anion such as F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, BPh₄⁻, ClO₄⁻, BF₄⁻, PF₆⁻, RSO₃⁻, RSO₄⁻, SO₄²⁻, CF₃SO₃⁻ or RCOO⁻;

if z is negative, Y is a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation; q = z/[charge Y];

L represents a ligand of general formula (B)



which contains at least five nitrogen atoms and in which the substituent groups R₁-R₅ are selected from hydrogen, hydroxy, halogen, nitroso, formyl, carboxyl, and esters and salts thereof, carbamoyl, sulfo, and esters

and salts hereof, sulfamoyl, nitro, amino, C₀-C₂₀-alkyl-hydroxy, C₀-C₂₀-alkyl-halogen, C₀-C₂₀-alkyl-nitroso, C₀-C₂₀-alkyl-formyl, C₀-C₂₀-alkyl-carboxyl, and esters and salts thereof, C₀-C₂₀-alkyl-carbamoyl, C₀-C₂₀-alkyl-sulfo, and esters and salts hereof, C₀-C₂₀-alkyl-sulfamoyl, C₀-C₂₀-alkyl-amino, C₀-C₂₀-alkylaryl, C₀-C₂₀-alkylheteroaryl, C₀-C₂₀ alkyl, C₀-C₈ alkoxy, carbonyl-C₀-C₆-alkoxy, and aryl-C₀-C₆-alkyl, provided that R₁ does not represent hydrogen.

2. Catalyst according to Claim 1, wherein L represents a ligand of general formula (B) in which the substituents R₂, R₃, R₄, R₅ are independently selected from C₀-C₅ alkyl substituted with a nitrogen-containing heterocyclic aromatic group, such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, thiazoles, triazoles and pyrimidines, or combinations thereof.
3. Catalyst according to Claim 2, wherein L represents a ligand of general formula (B) in which the substituent group R₁ represents C₀-C₂₀-alkylaryl, C₀-C₂₀-alkylheteroaryl, or C₀-C₂₀ alkyl.
4. Catalyst according to Claim 3, wherein L represents a ligand of general formula (B) in which the substituents groups R₂, R₃, R₄, R₅ are independently chosen from C₀-C₅ alkyl substituted with a pyridine ring.
5. Catalyst according to any of Claims 1-4, wherein X represents a co-ordinating species selected from CH₃CN, pyridine, H₂O, Cl⁻, OOH⁻ and OR⁻ wherein R is hydrogen, optionally substituted phenyl, naphthyl, or C₁-C₄ alkyl.
6. Catalyst according to any of Claims 1-5, wherein the counter ion Y is selected from RCOO⁻, BPh₄⁻, F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, BF₄⁻, PF₆⁻, RSO₃⁻, RSO₄⁻, SO₄²⁻ and NO₃⁻, wherein R=H, optionally substituted phenyl, naphthyl or C₁-C₄ alkyl.
7. Catalyst according to any of Claims 1-6, wherein the ligand L is N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane.
8. Catalyst according to any of Claims 1-6, wherein the ligand L is N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane.
9. A bleaching composition comprising a peroxy bleaching compound and a catalyst according to any of the preceding claims.
10. Composition according to claim 9, which comprises said peroxy bleaching compound at a level of from 2 to 35% by weight and said catalyst at a level corresponding to an iron content of from 0.0005 to 0.5% by weight.
11. Composition according to claim 9 or 10, wherein the peroxy bleaching compound is selected from hydrogen peroxide, hydrogen peroxide-liberating or generating compounds, peroxyacids and their salts, and mixtures thereof, optionally together with peroxyacid bleach precursors.
12. Composition according to any of claims 9-11, which further comprises a surface-active material, in an amount of from 10 to 50% by weight, and a detergency builder in an amount of from 5 to 80% by weight.